Silicon nanocrystals surface engineering by low-pressure plasmas andatmospheric-pressure microplasmas

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We present here two different plasma-based approaches to provide suitable surface characteristics for quantum confined silicon nanocrystals. Silicon nanocrystals are initially synthesized by electrochemical etching and by laser fragmentation in liquid. Subsequently we have used on one instance a microwave low-pressure plasma to grow carbon nanotubes using the silicon nanocrystals as catalyst particles. On a second instance we have used atmospheric-pressure microplasma technology to surface-passivate the silicon nanocrystals with C-based terminations. We will report on the processing and characterization details. In addition we will present results that relate to the suitability of these nanoscale building blocks for photovoltaic applications (e.g. photoluminescence, photoconductivity).

1. Introduction

Quantum confined silicon nanocrystals (SiNCs) may offer great opportunities in a wide range of applications due to several favorable characteristics. Firstly, silicon has limited environmental concerns, is considered a safe element and can rely on a well-established industrial know-how. Furthermore, silicon at the nanoscale is revealing interesting and useful properties that may trigger a second silicon revolution. The potential applications include photovoltaics, optoelectronics and health care technology [1-5].

However the control and synthesis of desired SiNCs surface characteristics are crucial for successful device integration and are currently fueling the debate on achieving accurate measurements of SiNCs properties.

We have therefore investigated the possibility of using carbon as the main element to provide desired surface functionalization and/or passivation. In the first case we have used SiNCs to catalyze the growth of carbon nanotubes (CNTs) in microwave low-pressure methane plasma. A second different approach has been to use atmospheric-pressure microplasma (AMP) [6-10] to provide C-terminations to SiNCs in ethanol dispersion.

2. Silicon nanocrystals for carbon nanotube growth

The silicon nanocrystals have been initially produced by electrochemical etching of a p-type and boron-doped silicon wafer (<100>, 0.1 Ω cm, thickness 0.525 mm) in HF:ethanol electrolyte (1:4) for 1 h at 1.6 mA cm^{-2} current density [11]. The SiNCs powder produced by this process was then subjected to laser fragmentation in water (Kr:F, 245 nm pulsed laser, 20 Hz, 10 ns at 1.94 W for 1 h and at room temperature) [12]. The fragmentation process induces the separation of the SiNCs that generally tend to aggregate in larger grains after electrochemical etching; in addition, surface passivation is improved as confirmed by photoluminescence measurements [13].

SiNCs were drop-cast on a silicon substrate from the aqueous SiNCs colloidal dispersion. The samples were left to dry in ambient atmosphere and therefore exposed to air before processing by microwave low-pressure plasma. The plasma process included a pretreatment of 3 minutes in nitrogen plasma (300 W, 20 mbar, 750 °C) followed by an Ar/CH_4 (3 to 1 ratio) plasma for 5 minutes at 600 W.

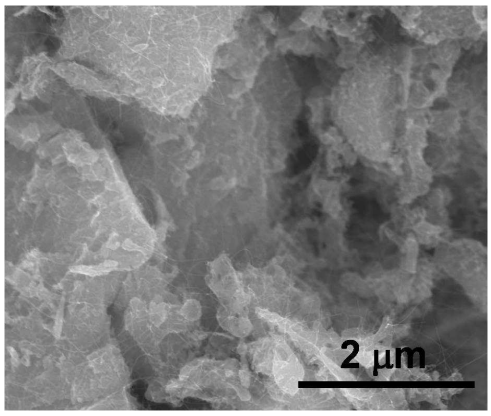

Fig. 1. Scanning Electron Microscopy image showing CNTs grown from SiNCs.

The plasma process produced filamentary structures (see Figure 1). These have been confirmed to be multi-walled CNTs by transmission electron microscopy (TEM) which also showed the presence of SiNCs located inside the CNTs.

The CNT growth is believed to be due to the specific surface characteristics formed after laser fragmentation. This is because the same plasma process applied to the as-prepared SiNCs after electrochemically etching did not produce the same results. It is well established that the electrochemical etching process forms H-terminated surfaces. At this time there is not conclusive evidence on the surface characteristics after laser fragmentation, however both photoluminescence and plasma processing indicate that the laser process induce significant changes that are also essential to CNT growth.

3. Microplasma surface functionalization of silicon nanocrystals

The SiNCs used in this case have been also produced by electrochemical etching at the same conditions as above. However, this time the SiNCs powder has not been subjected to laser fragmentation. Instead the powder has been dispersed in about 10 mL ethanol. The AMP was generated between a Ni tubing (0.6 mm external diameter and 0.3 mm internal diameter) and the surface of the ethanol-SiNCs colloidal dispersion (Figure 2).

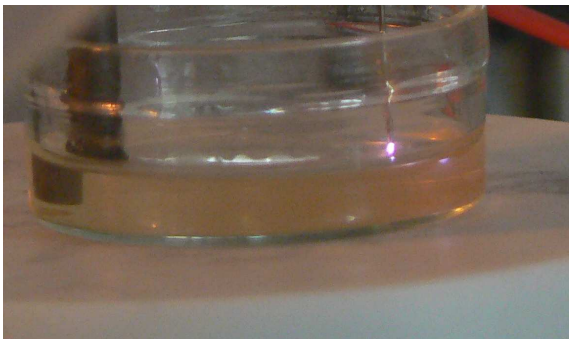

Fig. 2. Photograph of the AMP generated above the surface of the ethanol-SiNCs colloidal dispersion.

Argon was flown inside the Ni tubing at a rate of 25 sccm and a constant current of about 1.5 mA was applied. The discharge current was produced by applying a positive voltage at a carbon rod which was immersed in the dispersion (see on the left of Figure 2). The voltage was initially 2 kV and slowly decreased while processing to stable values just above 800 V. The circuit was completed by a 100 kΩ resistor between the Ni tubing and ground.

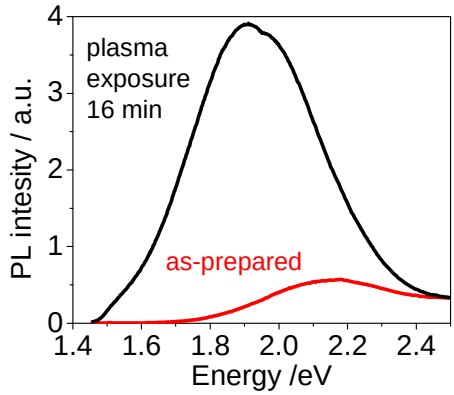

Fig. 3. Photoluminescence (PL) emission spectra of the SiNC dispersed in ethanol before and after DC plasma processing.

The process was applied to the colloidal dispersion for about 16 minutes and repeated several times. At the end of each 16-minute run the photoluminescence (PL) was measured. It is interesting to notice that while in the first 16-minute run, the SiNCs powder was observed to accumulate under the positive electrode (the carbon rod), after a few 16-minute runs, the powder began to group under the microplasma jet.

The PL measurements show that the maximum has been drastically increased and with a pronounced red-shift in the wavelength. Figure 3 shows the PL emission before microplasma processing and after the first 16-minute run. Although the specific mechanisms induced by this AMP process are still under investigation, it is clear that higher quality surface passivation has been produced. It is likely that surface charging of the SiNCs has contributed to chemical reactions promoting specific bindings. It has to be highlighted that the PL and therefore the surface characteristics are stable even after several days.

4. Conclusions

We have shown that laser fragmentation in water and microplasma processing can provide two different avenues for surface-engineered SiNCs. In the first case the surface characteristics have allowed CNT growth without metal catalysts. In the second case, AMP processing has induced modification of the surface characteristics with improved PL emission and improved passivation.

Acknowledgements

This work was partially supported by a NEDO Project (Japan). D.M. gratefully acknowledges the support of the JSPS Invitation Fellowship (Japan). The authors would also like to acknowledge the support of the Tyndall National Institute provided through the SFI-funded National Access Programme (NAP).

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